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A Kinetic Study of Propylene Metathesis over $\text{WO}_3\text{-SiO}_2$ Gel

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Recent workers have reported anomalous results for the metathesis of propylene over $\text{WO}_3\text{-SiO}_2$ gel in a flow system. One anomaly, confirmed in the present work, is an increase in catalytic activity with an increase in flow rate. The reaction was studied at a propylene partial pressure of 0.37-1 atm between 435 and 493°C. Two reaction mechanisms have recently been proposed; one includes a bimolecular surface step and the other is a carbene chain mechanism. The rate law for the carbene mechanism has been developed. Attempts were made to fit the catalytic activities to the rate laws for these two mechanisms. An attempt was also made to determine whether or not the activities meet the site density criterion. This criterion states for a postulated slow step that the calculated density of active sites on the surface, determined by analyzing kinetic data using transition state theory, must be a physically possible site density. Our results are consistent with the bimolecular, but not with the carbene, rate law. However, our data are not consistent with the site density criterion for the bimolecular rate law. The theoretical methods used enable us to detect anomalies in our kinetic data, in this case the flow rate anomaly. Applying the same tests to systems reported in the literature indicates that inconsistency with a rate law or a physically possible site density is not found when there is no flow rate anomaly.

INDEX DESCRIPTORS: metathesis mechanism, propylene metathesis, WO_3SiO_2 gel, metathesis kinetics.

The metathesis of propylene to ethylene and cis-2-butene occurs over many solid catalysts. Many of the catalysts for this reaction are mixed oxides, such as the oxides of molybdenum and aluminum; cobalt, molybdenum, and aluminum; tungsten and aluminum; and tungsten and silicon (1).

We are interested here in the behavior of the $\text{WO}_3\text{-SiO}_2$ gel catalyst. Moffat, Johnson, and Clark observed that this catalyst became more active with increased flow rate, and suggested that a very unusual mass transfer problem existed (2, 3). Moffat later suggested that the anomaly could be explained if there were very few, but very active, sites (4). This explanation was offered partly because of our conclusion that some catalysts have extremely low site densities (5, 6).

Luckner, McConchie, and Wills confirmed the anomalous results obtained with the $\text{WO}_3\text{-SiO}_2$ gel catalyst (7). They suggested that the problem arose because of a non-uniform impregnation of the silica gel support. They did not need to invoke a low site density to interpret their kinetic data and they were able to study the reaction under conditions such that there was no flow rate anomaly.

Several mechanisms for olefin metathesis have been proposed. These include various forms of a mechanism which includes a bimolecular surface step; one form is the so-called four-center mechanism, in which there is reaction between two olefin molecules adsorbed on adjacent pairs of sites. Recently, however, there has been considerable interest in a carbene mechanism, in which there is a chain reaction but not a bimolecular surface step. This mechanism has been suggested for heterogeneous and homogeneous liquid phase reactions and heterogeneous gas reactions (8-18), and is described in more detail in the Results and Discussion section.

In this paper we analyze the activity of a $\text{WO}_3\text{-SiO}_2$ catalyst for propylene metathesis. We have looked at the flow rate problem and have attempted to determine whether or not the results are consistent with any of the proposed mechanisms.

MATERIALS AND METHODS

Matheson C. P. propylene was used. No ethylene impurity was detected; the non- C_3 impurity was 0.09%. Both molecular sieve and Drierite drying tubes were used in the feed line. The catalyst, 6.9 wt % WO_3 on silica gel, of 200 m^2/g surface area, was provided by the Phillips Petroleum Company, and was used as 100-200 mesh powder. Nitrogen (used to flush the reactor and to dilute the propylene) was freed of oxygen impurity by by-passing it through a tube of hot

copper and subsequently dried in a molecular sieve drying tube.

A conventional, all-Pyrex differential flow reactor was used. The product was analyzed in an A-90-P Varian Gas Chromatograph, using a Porapak Q column and a tungsten filament thermal conductivity detector. In representative determinations, the ethylene:butene mole ratio averaged 1.05. The true value was taken to be 1; results are reported on the basis of ethylene analysis. The catalyst was normally pretreated with O_2 for 5 hrs. at 500°. During a run the activity of the catalyst increased for a period of about 2 hrs. and was then constant for at least 12 hrs. This "break-in" period has been observed by others. Westhoff and Moulijn concluded from gravimetric studies that the activity increase was due to a slight reduction of WO_3 by propylene, with no more than 1 oxygen atom in 60 removed during the induction period (19). We report only constant activities.

It was possible during a run to change the temperature, the partial pressure of propylene (P) by diluting with N_2 , and the flow rate and, after restoration of the original conditions, obtain the original activity. The thermal conversion was 0.2-0.3% at a flow rate of 10 ml/min and negligible at 40 ml/min. Activities reported were calculated after the thermal conversion was subtracted from the total conversion; the latter quantity was in the range 0.5-3.5%. Our error in measurement of activity, as determined from the average deviation in 7 paired determinations, was 3.4%.

RESULTS AND DISCUSSION

Activity as a function of flow rate for three different catalyst weights is given in Fig. 1. In Fig. 2, activity as a function of P is shown. Arrhenius plots of the activities are given in Fig. 3 for 4 flow rate-catalyst weight-pretreatment combinations.

Our results agree with others in that our activities increased with increasing flow rate. Pennella recently suggested that these anomalous results are not easily explained by an analysis of mass transfer (20). Pennella concluded for his system that reversible poison was introduced into the feed stream ahead of the catalyst bed at a rate independent of the flow rate. Thus, the partial pressure of the poison decreases, with an increase in activity, as the flow rate increases at constant total pressure. If poisoning is indeed a complicating factor, we might anticipate that the kinetic results for such a system cannot be reliably used in the elucidation of the reaction mechanism.

To pursue this matter further, we examine the two mechanisms for the reaction most recently proposed. We shall then examine rate data to

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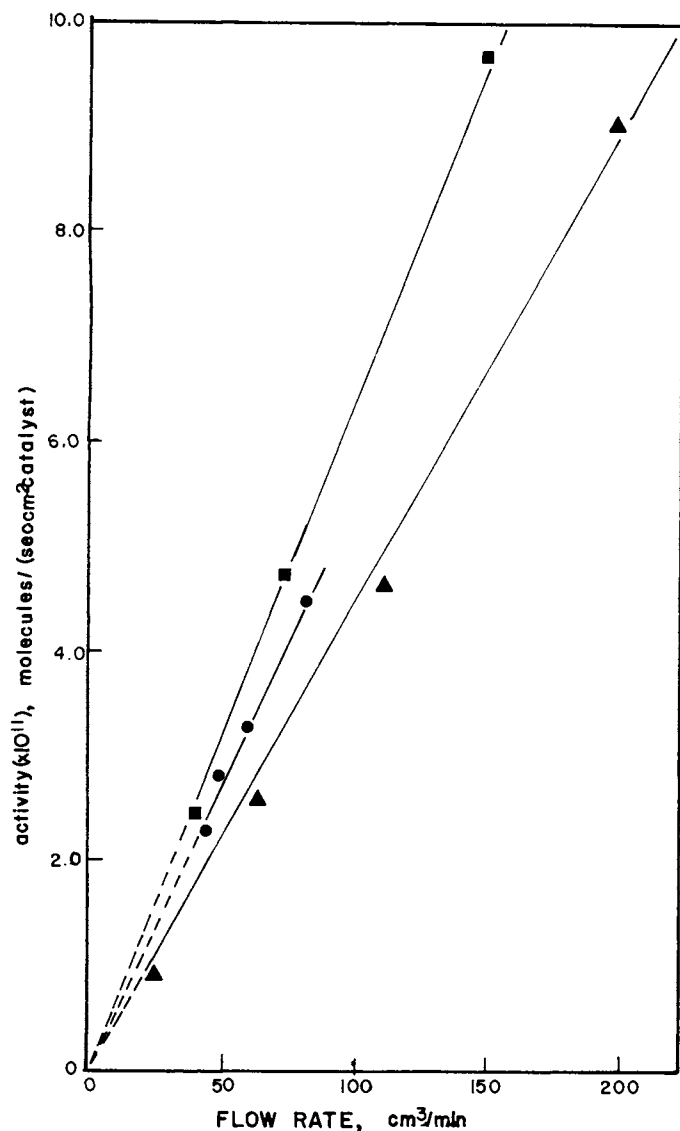


Fig. 1. Activity vs. flow rate. Square, 0.050. g catalyst. 475°; circle, 0.100 g catalyst, 466°; triangle, 1.00 g catalyst 477°.

determine whether either or both of the postulated mechanisms are possible.

The four-center mechanism

The kinetic scheme for this mechanism is that which applies to a bimolecular surface reaction; it is not necessary that there be four adjacent adsorption centers. Luckner, McConchie, and Wills show that the rate or catalyst activity, v , is then given by

$$v = kP^2 / (1 + KP)^2 \quad (1)$$

where P is the partial pressure of propylene and k and K are constants (7). Equation (1) can be rearranged to show that plots of $(P/v^{1/2})$ vs. P should be linear; and Luckner, McConchie, and Wills do obtain linear plots.

The carbene mechanism

For the carbene mechanism, a chain mechanism, various initiation

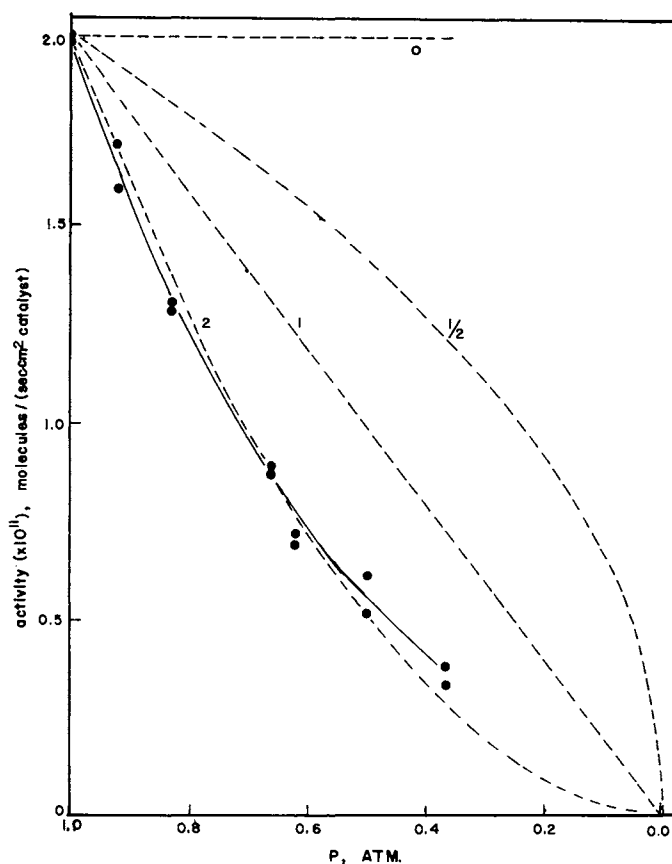
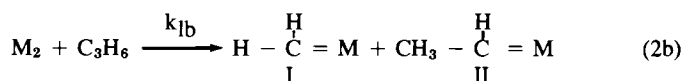
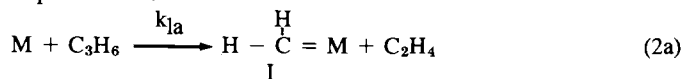
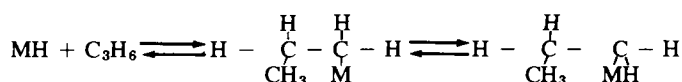


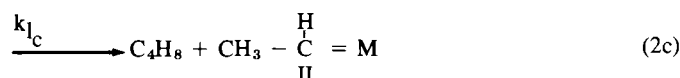
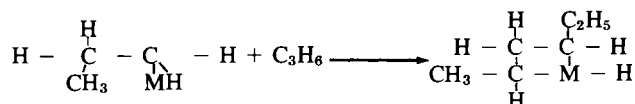
Fig. 2. Activity vs. partial pressure of propylene; temperature, 475°C; flow rate 10 ml/min; catalyst weight (normal pre-treat), 1.04 g. Circles and solid line, experimental; O, rate calculated if reaction is zero order; $1/2$, rate calculated if rate is proportional to $P^{1/2}$; 1, if proportional to P ; 2, if rate is given by Eq. 1. " $1/2$ " and "1" curves fitted to $P = 0$. $P = 1$ points; "2" curve fitted to $P = 0.67$. $P = 1$ points.

steps are conceivable:

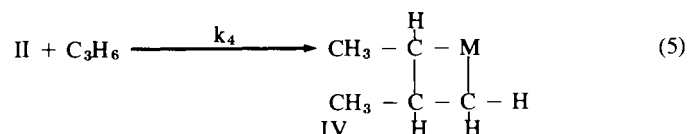
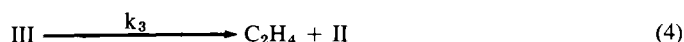
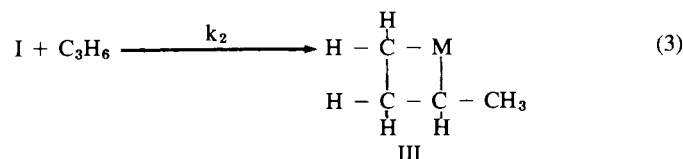


Either M or M_2 can be considered a site. (Where a metal-carbon bond is indicated in this development, no attempt is made to describe the bond polarity.) Lavery, Rooney, and Stewart suggest that the initiation step involves a metal hydride (15). Such an initiation can, in the case of propylene, be the following sequence, consisting of four steps:





Any one of the three reactions, (2a), (2b), or (2c), provides entry into the following chain. It is not necessary to differentiate between M, M₂, and MH; M is used in the description of the chain.



Reactions (3) and (5) each represent only one of the 2 ways propylene can react with species I and II. They can also react as follows:

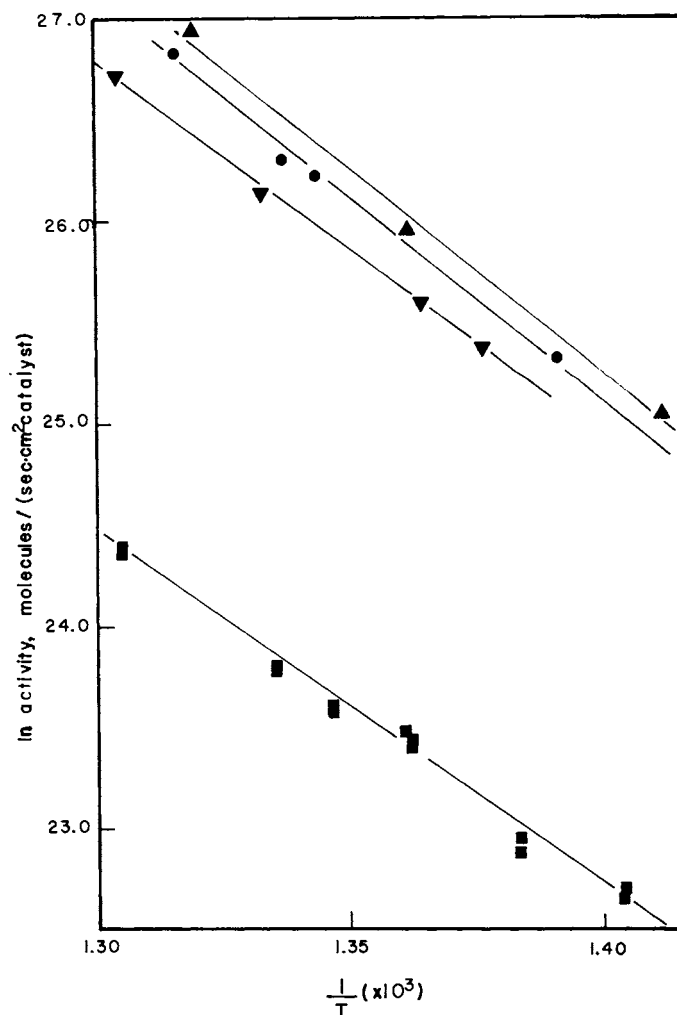
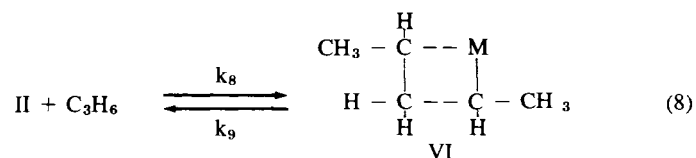
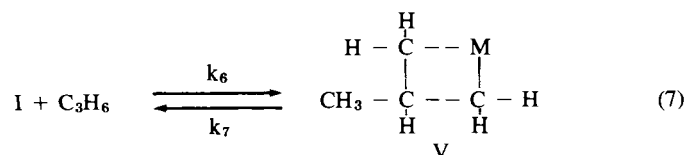


Fig. 3. Arrhenius plots. Symbol, How rate m ml/mm, wt. of catalyst m g. and activation energy in kcal/mole, respectively; triangle, 45.0. 100, 42; circle, 47, 0.050, 41; square, 10.1.04.39; inverted triangle, 45.0.250.36.1 atm. Partial pressure of propylene: 1 atm. Pretreatment: first three 6 hrs. O₂ at 600°C; fourth, 2 hrs. H₂ at 480 °C.

Thus, in reactions (3)-(8) there is shown 1 way to form and 1 way to decompose each of the 4 species III-VI. Note that the k_7 and k_9 steps are not necessarily the reverse of the k_6 and the k_8 steps in the usual sense: species V and VI can decompose to release different atoms than were added to the complex in the forward step.

We will now develop the steady state rate law for the carbene mechanism. It can be shown that the rate law is the same for each of the 3 initiation steps described; in the following, we use reaction (2a) as the initiation step. The steady state assumptions are the following:

$$\frac{d[\text{I}]}{dt} = 0 = -k_2 [\text{I}] \text{P} + k_3 [\text{IV}] - k_6 [\text{I}] \text{P} + k_7 [\text{V}] \quad (9)$$

$$\frac{d[\text{II}]}{dt} = 0 = k_3 [\text{III}] - k_4 [\text{II}] \text{P} - k_8 [\text{II}] \text{P} + k_9 [\text{VI}] \quad (10)$$

$$\frac{d[\text{III}]}{dt} = 0 = k_2 [\text{I}] P - k_3 [\text{III}] \quad (11)$$

$$\frac{d[\text{IV}]}{dt} = 0 = k_4 [\text{II}] P - k_5 [\text{IV}] \quad (12)$$

$$\frac{d[\text{V}]}{dt} = 0 = k_6 [\text{I}] P - k_7 [\text{V}] \quad (13)$$

$$\frac{d[\text{VI}]}{dt} = 0 = k_8 [\text{II}] P - k_9 [\text{VI}] \quad (14)$$

Since we are considering a chain reaction in the steady state, we can neglect the product formed in the initiation step. Butene and ethylene are produced in equal amounts; taking the rate of reaction to be the rate of ethylene production, we have from reaction (4),

$$v = k_3 [\text{III}] \quad (15)$$

If the active sites are taken to be those which have been activated by an initiation step, then the number of sites per cm^2 in the steady state is a constant and is given by

$$L = [\text{I}] + [\text{II}] + [\text{III}] + [\text{IV}] + [\text{V}] + [\text{VI}] \quad (16)$$

As we use Eq. (16) for the steady state, we assume either that every catalytic site is in one of the six forms, or that the only catalytic sites of interest are those that are in one of the six forms. In any case, the existence of a steady state implies that chain termination by destruction of a site is not an important factor. Therefore, in developing a rate law we do not need to consider the mechanism of chain termination or, for that matter, chain length.

Equations (9)-(16) can be combined to give the rate law for the carbene mechanism:

$$v = k_2 L \frac{P}{1 + (k_2/k_4) + P [(k_2/k_3) + (k_2/k_5) + (k_6/k_7) + (k_2 k_8/k_4 k_9)]} \quad (17)$$

Equation (17) is of the form

$$v = \frac{C_1 P}{C_2 + C_3 P} = \frac{(C_1/C_3)P}{(C_2/C_3) + P} = C_4 P/(C_5 + P) \quad (18)$$

where the C_i 's are constants. Thus, if the carbene mechanism is correct, the reaction is first order at low propylene partial pressure and zero order at high propylene partial pressure. (However, Katz and Rothchild reported for a somewhat related system that the carbene mechanism is consistent with a rate which is first order in olefin at high olefin concentration and higher order in olefin at low olefin concentration (11)). Since eq. (18) can be rearranged to give

$$(1/v) = (C_5/C_4)/P + 1/C_4 \quad (19)$$

a plot of $(1/v)$ vs. $(1/P)$ should be linear if the carbene mechanism is correct.

Test of the data

We show in Fig. 2 what v vs. P would be for various orders and/or mechanisms. When the reaction is zero order with the slow step unimolecular on a saturated surface, one-half order (adsorption accompanied by dissociation), and first order (where the slow step may be adsorption), the curves produced are the dashed lines labelled "0", " $1/2$ " and "1", respectively. The curve labelled "2" is v vs. P if Eq. (1) holds and the curve is fitted to the $P = 0.67$ and 1.0 atm points. The solid line approximates the experimental points; it is also the curve obtained if Eq. (18) holds. Here also the curve is fitted to the $P = 0.67$ and 1.0 atm points.

Inspection of Fig. 2 reveals that the curve for the carbene mechanism is slightly better than the "2" curve and much better than the others. It might therefore be concluded that the carbene mechanism is correct. There is, however, a difficulty which indicates that such a conclusion is not warranted. When the rates of Fig. 2 are plotted according to Eq. (19), the equation

$$1/v = (1.28 \times 10^{12}/P) - 8.4 \times 10^{11} \quad (20)$$

is obtained. The negative intercept is unacceptable. Either the carbene mechanism does not hold or, if it does, our data cannot be used to elucidate the mechanism. We believe that the anomaly reported in Fig. 1 may mean that our data cannot be used to determine the mechanism.

We have attempted to plot the rate data which Luckner, McConchie, and Wills report (in a figure) for a catalytic system which was similar to ours, except that they operated at flow rates high enough to eliminate the flow rate problem (7). For their results at 454°C in the 1-9 atm range, the $(1/v)$ vs. $(1/P)$ plot is apparently not far from linear and the intercept is positive, as required.

The site density criterion

The site density criterion, which we have described earlier, provides another means of determining whether or not rate data are consistent with a postulated slow step (21). We now develop the relation needed for a bimolecular surface reaction, such as the reaction associated with the four-center mechanism.

Transition state theory predicts that the rate of a bimolecular surface reaction is given by

$$v = \frac{(s/2) c_g c_g c_s^2}{L} \frac{kT}{h} \frac{f^\ddagger}{F_g F_g f_s} e^{-(E_0/RT)} \quad (21)$$

where the rate is given in molecules/ $(\text{cm}^2\text{-s})$, s is the number of sites adjacent to a given site, c_g and c_g , are the gas phase concentrations of the 2 reactants in molecules/ cm^3 , c_s is the number of bare sites/ cm^2 at any instant, L is the site density in sites/ cm^2 , k and h are the Boltzmann and Planck constants, respectively, T is the temperature, E_0 is the activation energy, R is the gas constant, and f_s , f^\ddagger , F_g , and F_g , are the partition functions for the bare site, the activated adsorbed species, and the two reactant gases, respectively (22). For a bimolecular reaction with but a single reactant, $c_g = c_g$, and $F_g = F_g$; Eq. (21) is then equivalent to Eq. (1) (22). Since the vibrational partition function is small, we assume that

$$F_g \approx F_{\text{tr}} F_{\text{rot}} \quad (22)$$

Table 1. Log L for propylene metathesis

| Catalyst | E, kcal/mole | T, °K | P, atm | v, molecules/cm ² -s | Log L ^a | | | Reference |
|--|-----------------|----------|-----------|------------------------------------|--------------------|-----|-------|--------------|
| | | | | | Step 1 | 3 | 5 | |
| 6.9 wt% WO ₃ -SiO ₂ | 39° | 748 | 1 | 2 × 10 ¹⁰ | 22 | 9 | 34 | Present work |
| 6.9 wt% WO ₃ -SiO ₂ | 20° | 748 | 1 | 2 × 10 ¹⁰ | 16 | 3 | 28 | b |
| 10 wt% WO ₃ -SiO ₂ | 16-28c | 727 | 1 | 1.1 × 10 ¹⁴ | 19-23 | 6-9 | 31-34 | 7 |
| 10 wt% WO ₃ -SiO ₂ | 13-18c | 727 | 9 | 6.0 × 10 ¹⁴ | 18-19 | 6-7 | 29-30 | 7 |
| Co/Mo/Al | 3.8-7.1c | 477 | 0.94 | 1.5 × 10 ¹³ | 15-16 | 2-3 | 26-27 | 24 |
| Mo (CO) ₆ /Al ₂ O ₃ | 7.3 | 342 | 0.016 | 5.6 × 10 ⁹ | 15 | 2 | 28 | 25 |
| Co/Mo/Al | 7.7 | 373 | 1 | 5.8 × 10 ¹⁴ d | 19 | 6 | 29 | 26 |

a

Step 1, bimolecular surface reaction of appreciably adsorbed propylene; Step 3, reaction of propylene on a saturated surface, zero order in propylene partial pressure; Step 5, bimolecular surface reaction between propylene molecules adsorbed on a sparsely covered surface. (Steps 3 and 5 refer to steps of the same number in Reference 21).

b

Hypothetical case; see text.

c

The range in activation energy is defined by the smallest and the largest values which can be calculated from the data.

d

Assuming a catalyst of 200 m²/g surface area and a reactor volume of 300 ml.

where F_{tr} and F_{rot} are the translational and rotational partition functions. Then we can rearrange Eq. (21), so that

$$c_s^2 = \frac{Lv (F_{tr}F_{rot})^2 f_s}{(s/2)c_g^2 (kT/h) f} e^{-E_0/RT} \quad (23)$$

In order to use Eq. (23) we need an expression for the adsorption isotherm of the reactant. For c_a molecules/cm² adsorbed we have

$$c_a = (c_s c_g) (f_a / (f_g f_s)) e^{-E_{ads}/RT} \quad (24)$$

where f_a is the partition function of the adsorbed molecule and E_{ads} its adsorption energy (22). By definition

$$L = c_a + c_s \quad (25)$$

Eliminating c_a from Eqs. (24) and (25) and rearranging, we have

$$c_s^2 = (L - c_s) (c_s / c_g) (f_s / f_a) (F_{tr}F_{rot}) e^{-E_{ads}/RT} \quad (26)$$

If we assume $f_a \approx f_s$, since both species involved are adsorbed, we can equate the right sides of Eqs. (23) and (26) and obtain

$$(1 - c_s / L) c_s = \frac{v F_{tr} F_{rot} e^{(E_0 + E_{ads})/RT}}{(s/2) c_g (kT/h)} \quad (27)$$

If the surface is 50% covered, i.e., if $c_s/L = 0.5$, the left side of Eq. (27) is at its maximum, 0.25 L; if the surface is either 10% or 90% covered, the left side is 0.09 L. Thus, if the surface is appreciably covered, somewhere between 10 and 90% covered, the right side of Eq. (27) can be used to estimate L, and the value obtained will be, assuming the coverage is between 10 and 90%, between nine and twenty five percent of the site density. In an Arrhenius plot, in which $\ln v$ is plotted against $(1/T)$, the apparent activation energy obtained from the slope is

actually equal to $(E_0 + E_{ads})$ if the pre-exponential factor is constant. It is seen from Eq. (27) that several variables, including a factor which is a function of the coverage, comprise the pre-exponential factor. It is normally assumed that the pre-exponential factor is constant. Arrhenius plots of our rates, using four different sets of conditions (Fig. 3), seem to justify the assumption that the pre-exponential factor is constant.

To use Eq. (27) we assume $1/2$ is the order of unity, as was possible in our earlier work (21); the apparent activation energy is determined from an Arrhenius plot, as in Fig. 3; to evaluate F_{rot} , the product of the 3 moments of inertia of propylene is needed; a value of $1.69 \times 10^{-115} \text{ g}^3 \text{ cm}^6$ was used (23). The value obtained for the right side of Eq. (27) is then multiplied by 4 (since the value obtained before multiplication is, as explained above, no greater than 0.25L) to obtain the minimum value of the site density. The results are given in Table 1 for our work (using an activation energy of 39 kcal/mole, the midpoint of the 36-42 kcal/mole range reported in Fig. 3), for the results using a similar WO₃-SiO₂ gel catalyst used by Luckner, McConchie, and Wills (7), and for results on 3 non-WO₃-SiO₂ gel catalysts reported in the literature (24-26).

We report in Table 1 log L values (rounded off to the nearest integer because the method and the assumptions used preclude the use of a greater number of significant figures) which we have calculated for 3 mechanisms — the bimolecular, appreciably adsorbed case which has been described, a mechanism in which the rate is zero order in propylene and the slow step is a unimolecular surface step, and a bimolecular case in which the surface is sparsely covered. (The methods of calculation used for the latter two mechanisms are given in Reference 21. For each assumed mechanism, the activation energy or the energy in the exponential factor such as that of Eq. (27), is the observed activation energy, obtained from an Arrhenius plot.)

For the carbene mechanism it can be shown (cf. Eqs. (17)-(19)) that evaluation of the slope and the intercept in a plot of $(1/v)$ vs. $(1/P)$ can provide the value of $(k_2 k_4 L)/(k_2 + k_4)$. From an inspection of reactions (3) and (5), it seems likely that

$$k_2 \approx k_4 \quad (28)$$

and therefore an approximate value of $k_2 L$ or $k_4 L$ could be obtained. Reactions (3) and (5) are adsorption steps for which L can be evaluated

if k_2L (or k_4L) is known at different temperatures (21). We cannot report L values for the carbene mechanism using our data because, as noted above, of the unacceptable intercept in a plot of Eq. (20).

For some systems reported in Table 1 we use the extreme values of the activation energy which can be calculated from the reported data in order that the bias introduced by the method of treating the data be minimal. Wherever the extreme values of the activation energy are used, the smallest log L value corresponds to the smallest value of the activation energy.

It is physically impossible for a catalyst to have more than about 10^{15} sites/cm²; in some cases, there may be as few as 10^7 - 10^8 sites/cm² (5, 6). Luckner, McConchie, and Wills report that the reaction approaches zero order at 9 atm but is far from zero order at 1 atm, in agreement with what we found at 1 atm. (7). Therefore, for the W_0_3 - SiO_2 gel catalysts the zero order (Step 3) calculation has relevance only for the results at 9 atm in Table 1; in the other W_0_3 - SiO_2 gel cases, only Step 1 (bimolecular, appreciably adsorbed) and Step 5 (bimolecular, sparsely covered) may be considered.

Except for the "hypothetical" case, the log L values for the W_0_3 - SiO_2 gel catalysts are at best on the borderline of being physically acceptable. The hypothetical case shows how much our activation energy would have to change in order to produce a log L value (of 16) which would be close to that which is physically possible.

Peculiar flow rate, poison, etc. problems have not been reported for propylene metathesis over catalysts other than W_0_3 - SiO_2 gel. For such catalysts we might expect to find physically acceptable log L values using the method described if log L can be calculated for the correct mechanism. Kinetic results and log L values for three such systems are also given in Table 1. For two of them, the fifth and sixth entries of Table 1, the log L values for the bimolecular, appreciably adsorbed slow step are quite acceptable. For the last entry the reaction is zero order in propylene partial pressure and therefore Step 3 should be considered (26). The low site density obtained (10^6 sites/cm²) is on the borderline of being physically acceptable; the low value is possibly accounted for by the approximations of the method and the necessity of estimating the catalyst surface area and the reactor volume.

Conclusions

Our results for propylene metathesis over W_0_3 - SiO_2 are inconsistent with the carbene rate law and any rate laws which predict the reaction to be zero, one-half, or first order over the entire range of propylene partial pressure which we studied. In addition, application of the site density criterion indicates that our results are not consistent with a mechanism involving a bimolecular surface reaction. It is quite possible that our inability to show that our experimental results are consistent with at least one postulated mechanism is related to the flow rate problem shown in Fig. 1. If we had at our disposal only the experimental results of Figs. 2 and 3, it might seem at first that nothing is unusual. What we have demonstrated is that there are theoretical means of testing for consistency the data of Figs. 2 and 3, using Eq. (19) and the equations used to develop the log L values of Table 1, including Eq. (27).

For the similar system studied by Luckner, McConchie, and Wills, where there was not, however, a flow rate problem, we have demonstrated (Table 1) that both a zero order and a bimolecular surface mechanism seem unlikely, but that the carbene mechanism, using Eq. (19) to test their data, is possible. For the last three systems listed in Table 1, we have suggested possible mechanisms, but in each case the authors have not reported enough data to permit the carbene mechanism to be tested using Eq. (19).

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